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Extraction of Interaction Energies From Scanning Tunneling Microscopy and Field–Ion Microscopy Data

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ABSTRACT

The extraction of adatom–adatom interaction energies from STM and FIM images is discussed. For the case of comparing experimental data with a solved model (*e.g.* Monte–Carlo simulations), an expression for the expected precision is derived. It is demonstrated that in the absence of any Monte–Carlo calculations the interaction energies can be extracted if measurements are made at more than one temperature. The relative uncertainty in the determination of the interaction energies for the case of a solved *vs.* an unsolved model as a function of system size and temperature is presented.

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The interactions among adsorbates on surfaces are of fundamental interest. Adatom–adatom interactions play an important role in (among other things) two–dimensional phase transitions, the formation of surface layer superstructures, surface reactions and adsorption and desorption phenomena. Interaction energies have typically been studied with macroscopic techniques such as LEED (low energy electron diffraction), TPD (temperature programmed desorption), isobars, isotherms, and heat capacity measurements which average over thousands of atoms. The microscopic parameters are subsequently extracted by fitting the macroscopically averaged experimental data to some postulated model. An Arrhenius–type analysis is typically used for kinetic data[1,2] while Monte Carlo simulations are often useful for analyzing equilibrium measurements.[3,4,5]

Field ion microscopy (FIM) and scanning tunneling microscopy (STM) are techniques which give real space images with atomic resolution. The data of interest here are snapshots of the atomic positions of the adsorbate and substrate atoms. Given this type of information, statistical mechanics can be used to analyze the data directly. The probability of observing the system in a given energy state E_i at a temperature T is:

$$P(E_i, T) = \frac{g(E_i)exp(\frac{-E_i}{kT})}{Q(T)} \qquad 1)$$

where g is the number of ways of arranging the adatoms on the surfaces such that the energy is E_i (the degeneracy), k is Boltzmann's constant, and Q is the partition function.

The discussion here is in terms of the lattice gas model, in which case g becomes the configurational degeneracy. If the internal states of the actual system (vibrational, etc.) are nearly the same for all configurations, or if the energies associated with these modes are small compared with the configurational energies, then the lattice gas model holds to a good approximation.

Interaction energies have previously been extracted from FIM data by limiting the number of adsorbates studied at one time (usually to just two).[6] In this case it is easy to calculate analytically the degeneracy and thus extract the energies.[7] For the case of STM data, the system size and number of adatoms are typically large, which makes the degeneracy incalculable for all but the simplest systems. In this case Monte Carlo calculations have been used for extracting interaction energies: the

interaction energies in the simulation are adjusted until the computer generated images correlate with the STM images.[4]

In this letter a technique is presented which allows for the calculation of interaction energies without the need for calculating the degeneracies. This technique is useful for analyzing snapshots of many interacting adatoms which greatly increases the information per snapshot from the case of only two adatoms. The outline of the rest of the letter is as follows. First, the model is presented for an arbitrary type and number of interactions. Next, the temperature and system size dependencies of the expected uncertainty of the extracted energy is derived for the lattice gas Ising system. Finally, the uncertainties obtained with this technique are compared to those obtained for the case of comparing real space images to Monte Carlo simulations.

The data required for this technique are a large set of real space snapshots of the system at two (or more) different temperatures. The fluctuations in the energy of the system[8] at the two temperatures are exploited to extract the interaction energies. The first step is to hypothesize a set of interaction types to be explored. There is no limit to the number or type of possible interactions: *i.e.* nearest neighbor, next nearest neighbor, three body interactions etc.. For any set of interactions the total configurational energy of the system can be written as:

$$E_i = \Sigma_j \, N_j \omega_j \qquad 2)$$

where N_j is the number of neighbors of type j, and ω_j is the strength of the jth interaction, which is to be determined.

The probability of observing the system with a given set of neighbors $\{N_j\}$ at a temperature T_a is

$$P(\{N_j\}, T_a) = \frac{g(\{N_j\}) exp(-\frac{\Sigma_j N_j \omega_j}{kT_a})}{Q(T_a)} \sim \frac{n(\{N_j\}, T_a)}{\Sigma_l n(\{N_j\}, T_a)} \qquad 3)$$

where $n(\{N_j\},T)$ is the number of experimental observations of the system in a state with $\{N_j\}$ neighbors. The approximation becomes more exact as the total number of measurements, $\Sigma_l n(\{N_j\},T)$, increases. By taking the ratio of the two probability distributions at each value of $\{N_j\}$, the degeneracy term, g, is eliminated. The various interaction energies are found by curve

fitting the data; if one of the hypothesized interactions do not actually exist a small value will be returned for the corresponding parameter.

If the two temperatures are equal no information about the interaction energy can be gained (without solving the model); also, if the two temperatures are far apart the overlap between the two probability distributions is small and little information can be extracted. This implies that there exists optimum temperatures at which to investigate the system. To explore this, the Ising model is used for computational convenience. The problem can be stated: given that only nearest neighbor interactions are important and without using any Monte Carlo simulations or knowledge of the solved model, at what two temperatures should the system be observed in order to extract the interaction parameter with the highest degree of precision?

The parent distributions from which measurements are to be taken are given by equation 3 for T_a and T_b, where J is the actual interaction energy and {Nj} is number of nearest neighbors (N_1). The ratio of the number of observations of N_1 at the two temperatures is least squares fit to determine the best estimate of the interaction parameter ω. The sum of the squares of the residuals is:

$$X^2 = \sum_{N1} \frac{1}{\sigma_{N1}^2} \left[\frac{n(N_1, T_a)}{n(N_1, T_b)} - \exp\left(\frac{-N_1 \omega}{k} \left(\frac{1}{T_a} - \frac{1}{T_b} \right) \right) \frac{Q(\omega, T_b)}{Q(\omega, T_a)} \right]^2 \qquad 4)$$

Since the ratio of the partition functions (Q_b/Q_a) must also be treated as a parameter, the best value of ω is found using a two parameter fit:

$$\frac{dX^2}{d\omega} = \frac{dX^2}{d\left(\frac{Q_b}{Q_a}\right)} = 0$$

The error in the determination of ω is given by:[9]

$$\sigma_\omega = \left[\frac{D_{Q'Q'}}{D_{\omega\omega}\, D_{Q'Q'} - (D_{Q'\omega})^2} \right]^{1/2} \qquad 5)$$

where

$$D_{xy} = \frac{1}{2} \frac{d^2 X^2}{dx dy} \qquad \text{and} \qquad Q' = \frac{Q_b}{Q_a}$$

In the limit of a large number of snapshots, ω and Q' can be determined exactly, that is

$$\frac{n(N_1,T_a)}{n(N_1,T_b)}-\exp\left(\frac{-N_1\omega}{k}\left(\frac{1}{T_a}-\frac{1}{T_b}\right)\right)\frac{Q(\omega,T_b)}{Q(\omega,T_a)}=0 \qquad 6)$$

for every N_1.

Using the above equations σ_ω/ω for different size Ising systems can easily be calculated. These are plotted in figure 1 as a function of T_a and T_b and in figure 2 as a function of T_a with constant T_b, assuming that the same number of measurements are taken at both temperatures. There are several important features shown in these figures: 1) the line $T_a=T_b$ has σ_ω equal to infinite, as expected, 2) for higher temperatures the curves in figure 1 become parallel to the temperature axes, 3) the temperature range over which the interaction parameter can be extracted is larger for smaller systems, and 4) the two optimum temperatures move closer together and towards the temperature at which the heat capacity is a maximum as the system size increases. These results are particularly important in light of the recent developments in STM which allow the system size to be controlled by building "corrals" for adatoms[10].

It is now useful to compare the expected error in the determination of the interaction energy for a solved, (known g), *vs.* an unsolved model. For the case of a solved model the experimental energy distribution is compared to the calculated distribution (*e.g.* through Monte Carlo simulation). The analysis will be given for a system with a single (but arbitrary) interaction type. The parent distribution from which measurements are taken is given by equation 3 with $\{N_j\}=N_1$. The experimental data would consist of the set of $n(N_1,T)$ which is, as above, the number of observations of the system having N_1 neighbors at a given temperature. A least square analysis is again used, in this case with only one adjustable parameter. The sum of the squares of the residual is

$$X^2=\sum_{N_1}\frac{1}{\sigma_{N1}^2}\left[n(N_1,T)-\frac{g(N_1)\exp\left(\frac{-N_1\omega}{kT}\right)}{Q(T)}\right]^2 \qquad 7)$$

The error in the determination of the interaction energy is obtained as above; giving for a solved model

$$\frac{\sigma_\omega}{\omega}=\sqrt{\frac{k}{nC}} \qquad 8)$$

where n is the number of measurements and C is the heat capacity. This simple but important result

shows that the most information about the interaction energy is contained at the heat capacity maximum and falls off as $1/\sqrt{C}$.

Using equations 6 and 8, the ratio of the total number of measurements required to obtain the interaction energy to a specified accuracy for the case of an unsolved model (the new model presented here) to the case of a solved (Ising) model can be determined. This is shown in figure 3) as a function of system size, assuming that all measurements are taken at optimum temperatures. For large system this ratio seems to approach ~2.6.

For two interactions it is easy to show that the uncertainty in the determination of the interaction energies are

$$\frac{\sigma_{\omega_1}}{\omega_1} = \sqrt{(\frac{k}{n})(\frac{C_{22}}{C_{11}C_{22}-C_{12}})} \qquad 9)$$

where n is again the total number of measurements and

$$C_{ij} \equiv \frac{1}{kT^2}(< N_iN_j > - < N_i >< N_j >)$$

Notice that if $C_{12} = 0$ then equation 9 revert to equation 8. This result shows that for each interaction parameter there is an optimum temperature at which to measure. Analogous results are easily obtained for any number of interactions.

It has been demonstrated that, without running Monte Carlo simulations or otherwise solving the model, interaction energies can be extracted from real space images if measurements are taken at more than one temperature. Furthermore, a limit for the accuracy of the determination of interaction parameters for a solved model as a function of number of measurements was derived. Finally, the additional information gained about the interaction energy by running Monte Carlo simulations has been quantified. Future work in this area includes: 1) more complicated models, 2) the advantage of taking data at more temperatures, and 3) the optimum search for the correct model (interaction types and strengths), both with Monte Carlo simulations and with the technique introduced here.

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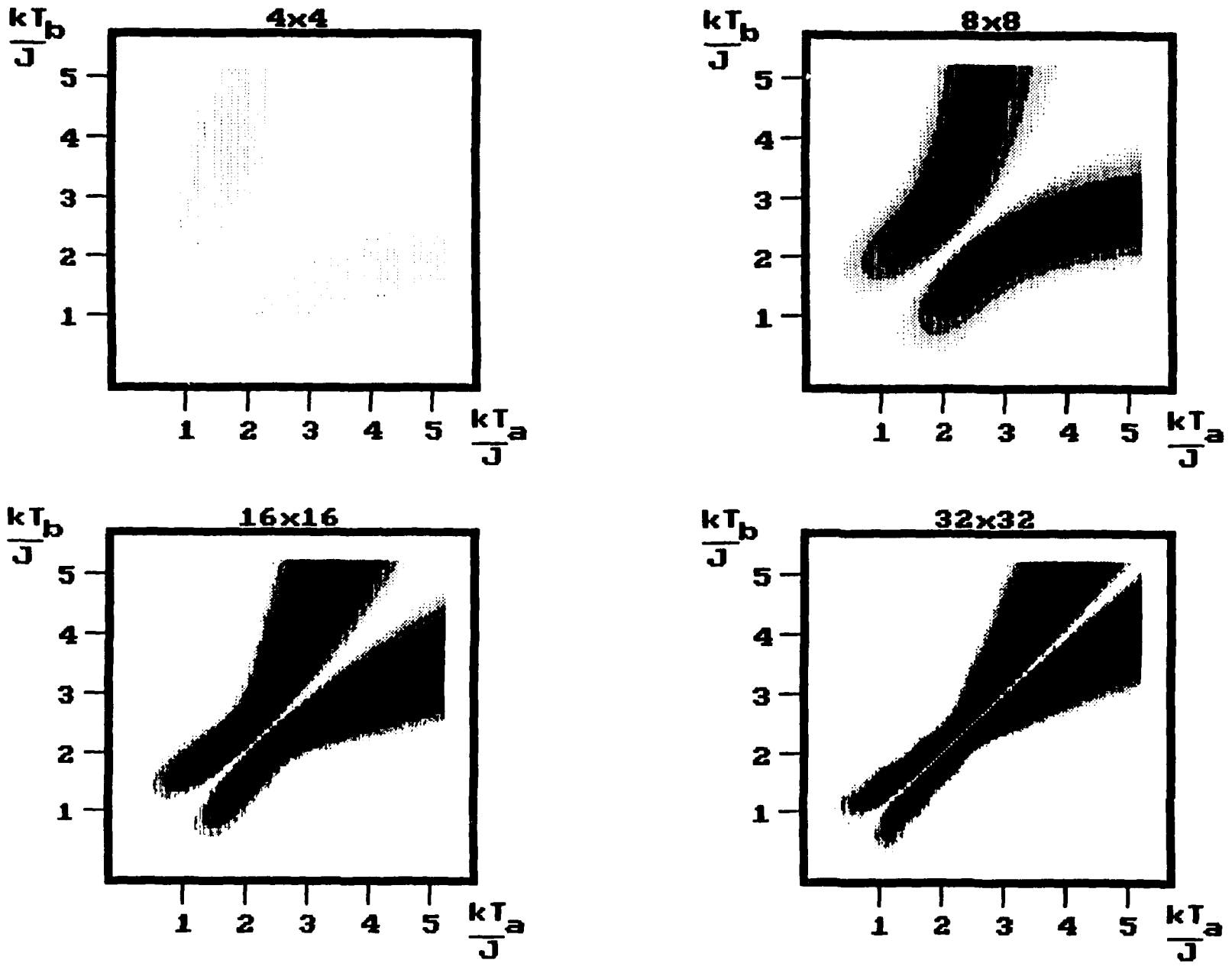
FIGURE CAPTIONS

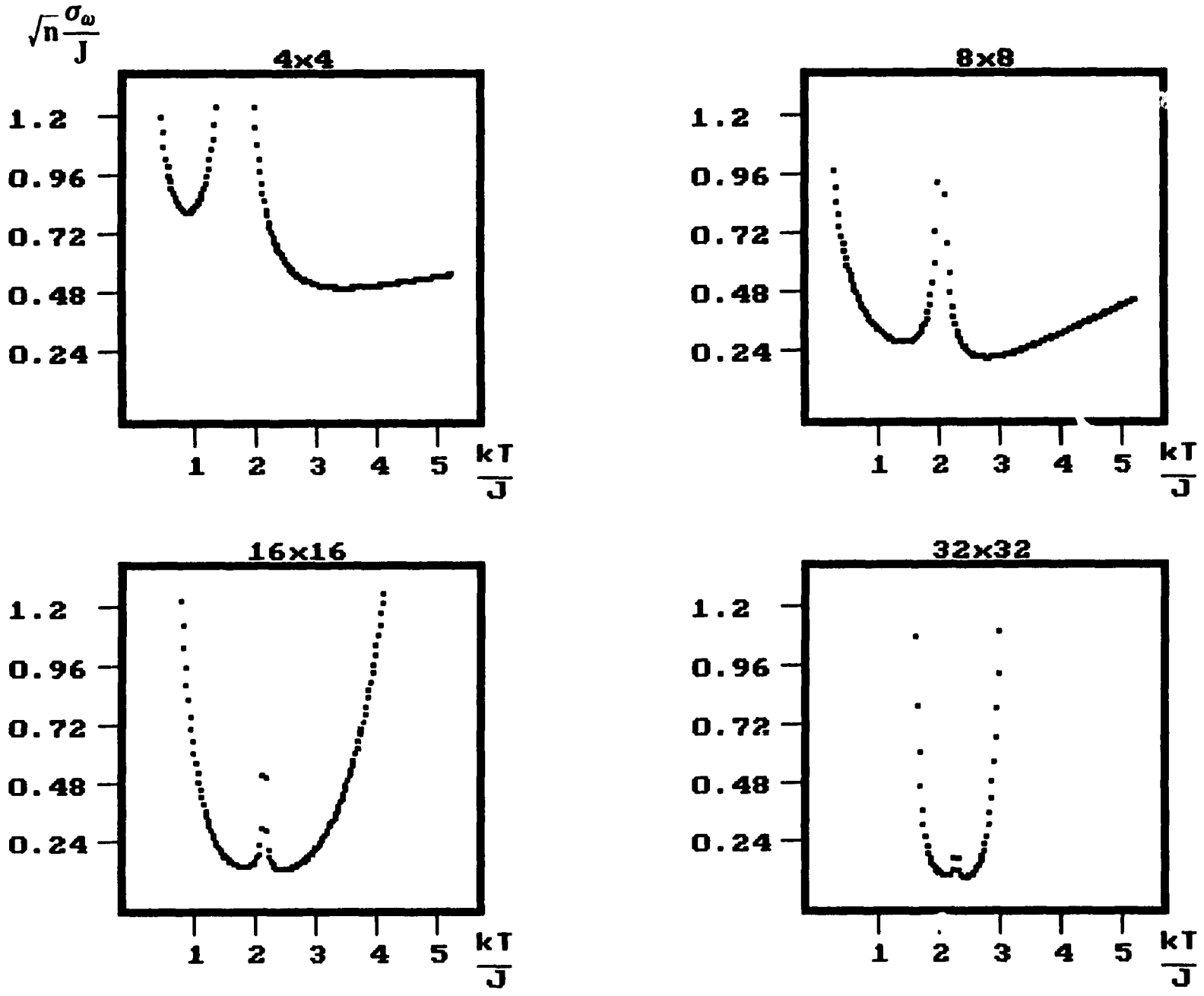
Figure 1) A gray scale of $\sigma\omega/\omega$ *vs.* T_a and T_b for four different size Ising systems determined as per equation 6). Darker indicates a lower value of $\sigma\omega$. Notice that along $T_a = T_b$, $\sigma\omega$ equals infinity.

Figure 2) $\sigma\omega/\omega$ vs. T_a (with T_b optimized) for four different size Ising systems. These are simply cross sections through the graphs in figure 1. The range of temperatures over which the interaction parameter can be extracted is larger for smaller systems. This is simply due to the fact that there are greater fluctuations for smaller systems.

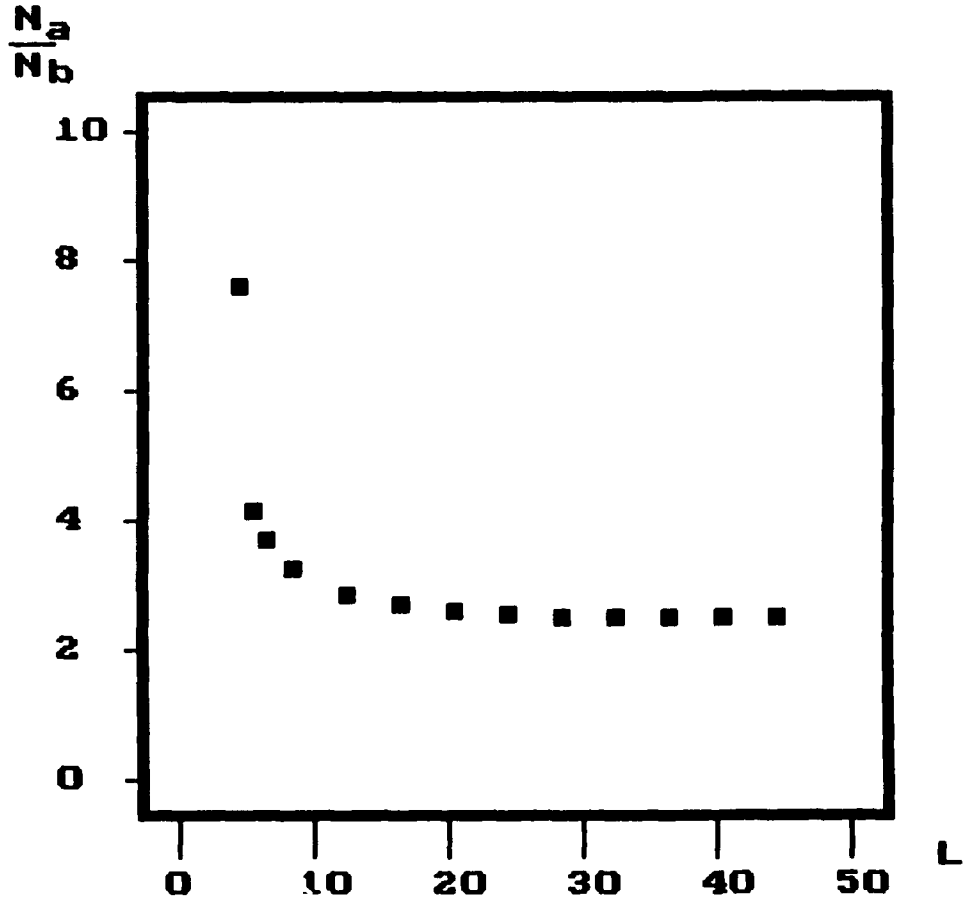
Figure 3) The ratio of N_a/N_b as a function of system size (LxL). N_a is the number of measurements required to obtain the interaction parameter to a certain degree of precision using the technique introduced here. N_b is the number of measurements required to obtain this parameter to the same precision if Monte Carlo calculations are used. If Monte Carlo calculations are carried out then roughly a factor of 2.6 fewer snapshots are required to determine the interaction energy to the same precision as in the absence of calculations (for systems $\gtrsim$ 16x16).



Meyer figure 1



Meyer figure 2



Meyer figure 3